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ORIGINAL PAPER

Preparation and phase transition characterization of VO_2 thin film on single crystal Si (100) substrate by sol–gel process

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Abstract Vanadium dioxide (VO_2) thin films were fabricated on single crystal Si (100) substrates by sol–gel method, including a process of annealing a vanadium pentoxide (V_2O_5) gel precursor at different temperatures. The crystalline structure and morphology of the films were investigated by XRD, FE-SEM and AFM, indicating that the films underwent the grain growth, agglomeration and grain refinement process with increased annealing temperatures. The film annealed at 500 °C exhibits the formation of VO_2 phase with a strong (011) preferred orientation and high crystallinity, the surface of the film is uniform and compact with a grain size of about 120 nm. Meanwhile, the film exhibits excellent phase transition properties, with a decrease of transmittance from 35.5 to 2.5% at $\lambda = 25$ μm and more than 3 orders of resistivity magnitude variation bellow and above the phase transition temperature. The phase transition temperature is evaluated at 60.4 °C in the heating transition and 55.8 °C in the cooling transition. Furthermore, the phase transition property of the VO_2 film appears to be able to remain stable over repetitive cycles 100 times.

Keywords VO_2 thin film · Sol–gel · Single crystal Si substrate · Phase transition

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1 Introduction

Vanadium dioxide (VO_2) is a transition-metal oxide that undergoes a reversible first order phase transition from a low temperature semiconductor phase to a high temperature metal phase nearly 68 °C, which can be manipulated by doping or stress [1, 2]. The transition is accompanied by significant and abrupt change in optical and electrical properties [3, 4]. Recently, it has been observed that this phase transition can be triggered by not only temperature, but also electric field, light and pressure [5–7]. All these properties make VO_2 as a candidate material for a variety of applications, such as thermochromic windows, IR uncooled bolometer, optical switching, and sensor devices [8–11]. Wherein, the electric field triggered phase transition in VO_2 is particularly suitable for applications as electrical switching, modulator and memory devices [12, 13].

Single crystal Si is one of the most frequently used substrates in VO_2-based devices due to its well-known electrical properties and low price. Moreover, the high-purity Si has been demonstrated to be not only the most transparent but also the least dispersive medium in the terahertz region, and hence is especially applicable as substrate contacts in VO_2-based THz devices [14, 15]. Several methods including pulse laser deposition, reactive sputtering, chemical vapor deposition and sol–gel method have been used to deposit VO_2 films. Of these methods, the sol–gel process is regarded as a quite promising and important method because of its low cost, easy coating of large-scale surface, flexible control of film thickness, and many other advantages [16–18]. However, it is usually difficult to obtain a good film of VO_2 on Si substrate by sol–gel process, for their bad contact performance induced by the lack of hydrophilic nature of Si interface.

In this research, we described the fabrication of VO_2 films on crystalline Si substrate using a sol–gel method

followed by an annealing process at different temperatures. The Si substrate was pre-treated with hydrophilic solution and obtained an improved hydrophilicity, which resulted in a better contact performance between the film and Si substrate. The crystalline structure and morphology of the films were studied using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Moreover, the phase transition properties were investigated using an FT-IR method and a resistivity measurement system.

2 Experiments

2.1 Surface cleaning and hydrophilic treatment of Silicon substrate

In a surface treatment, the n-type single crystal Si (100) substrate ($\sim$2000 Ω cm resistivity, Hefei Kejing Materials Technology Co., Ltd., China) was first pre-treated by ultrasonic cleaning in ethyl alcohol for 30 min and rinsing with de-ionized (DI) water for 5 min, in order to remove some organic contaminations on the surface. And then a thin SiO_x layer was formed by oxidizing the Si substrate in the hydrophilic solution composed of mixture of concentrated H_2SO_4 and H_2O_2 with a ratio of 1:1 at 90 °C for 120 min. Through the treatment, the Si surface underwent surface functionalization through hydroxylation [19]. The cation impurities could be also removed in this treatment. After these treatments, the substrate was rinsed again with DI water for 5 min, and blown dry at 60 °C for 15 min.

2.2 Sample preparation

We prepared V_2O_5 sol with a method described in the previous paper [20], in which the melting V_2O_5 underwent hydrolysis and polycondensation reaction to form a colloid. The sol then evolved toward the formation of inorganic network (gel) [21]. According to Ref. [22], the V_2O_5 gels obtained a structure as described in Fig. 1. Following by water adsorption and dissociation occurs at the oxide–water interface leading to the acid dissociation of V–OH groups, the V_2O_5 gels could then be described as polyvanadic acids $H_xV_2O_5$. We proved this model in a later subsection.

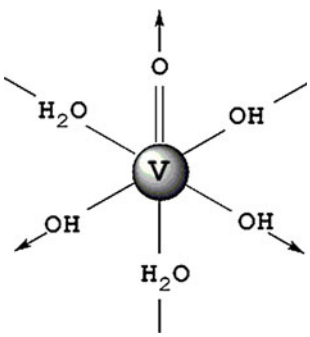

Fig. 1 Structure representation of the V_2O_5 gel

The precursor films were deposited on Si (100) substrate by dip coating method. Then the films were dried around 90 °C for 15 min to remove the residual moisture. The dip coating process was repeated to increase the film thickness. The binding of V_2O_5 gel with Si substrate includes two approaches: a direct adsorption and a chemical linker, which was similar to the phenomena reported in Ref. [23]. The chemical linker provided a nearly covalent-strength bond between the gel and the surface due to the hydroxylation of Si interface.

In order to form the VO_2 films, subsequent annealing was done in a furnace at the temperatures of 110, 300, 500 and 700 °C for 1.5 h in a static atmosphere of nitrogen, with a heating rate of 8 °C min^{-1}. The resulting films with a thickness of about 150 nm were obtained after cooling down from the annealing temperature.

2.3 Characterizations

Contact angles with DI water were performed by a pendant-drop method with an automatic contact angle analyzer combined with a flash camera equipment (DSA 100, Kruss, Germany) at room temperature. The reported measurements are averages of five contact angle measurements recorded on each sample.

Functional groups of the V_2O_5 gel were analyzed by FT-IR spectrometer (Tensor 27, Bruker, Germany) to confirm the existence of –OH groups. The resolution of detection was set as 4 cm^{-1}. The sample was acquired by spreading the gel on KBr plates, and then measured after different roasting time at 110 °C.

Crystalline structure of the films was determined by XRD (X' Pert, Philips) with Cu Kα ($\lambda = 0.15406$ nm) radiation source.

Surface morphology was studied by FE-SEM (Inspect F, FEI, Holland) with an accelerating voltage of 20 kV. The magnifying power was 80 000x. The morphology was also investigated by AFM (Nanoscope Multimode APM, Vecco Instrument, America) with a tapping mode under ambient conditions. Etched Si nanoprobe tip with spring constant of 40 N m^{-1} was used.

Optical properties of the films were investigated by FT-IR spectrometer to analyze the transmittance of the films at the middle infrared range bellow and above the VO_2 phase transition temperature.

Electrical resistivity dependent on the temperature was measured by the conventional four-point probe method combined with a heater element.

3 Results and discussion

3.1 Contact angles

The Si substrate with no hydrophilic treatment has bad hydrophilicity and the contact angle is about 68.0° (t = 0 min). With the oxidization of the Si surface, the contact angle decreased obviously and showed a value of 12.1° after a 120 min oxidizing treatment, indicating a significant enhanced hydrophilicity. It was attributed to the increased compactness of SiO_2 layer, followed by a combination of –OH groups on the substrate surface. The Si–OH groups increase the surface energy and then improve the hydrophilicity of Si surface.

3.2 FT-IR spectrum of V_2O_5 gel

The V_2O_5 gel is an inorganic network derived from hydrolysis and polycondensation reaction of melting V_2O_5 in DI water. Figure 2 shows the FT-IR spectra of the gel on KBr plates in the spectral range 4,000–400 cm^{-1}. A broad peak below 850 cm^{-1} could be assigned to characteristic distribution of V–O groups. Moreover, two strong peaks at 3,460 and 1,639 cm^{-1} correspond to stretching vibration and bending vibration bands of -OH groups respectively, which could be assigned to water absorption or due to chemical bonding of -OH groups in the V_2O_5 gel. The intensity of these two peaks versus the roasting time at 110 °C shows a tendency of reduction, denoting a consumption of -OH groups with roasting. However, the two peaks still exist after roasting 10 min indicating a chemical bonding of –OH groups.

Furthermore, we tested the PH of the V_2O_5 gel, and observed a value in the range of 0.5–1.0, which means a strong acid. It could be explained by the acid dissociation of V–OH groups in the gel system. All these results confirm the gel structure existing in the form of polyvanadic acids $H_xV_2O_5$ as described in Fig. 1.

3.3 XRD

Figure 3 shows XRD patterns of VO_x films annealed at various temperatures. As seen in Fig. 3a, only one broad peak extending from 20° to 27° is observed for the sample annealed at 110 °C. It means the film is still amorphous. The XRD pattern of the film annealed at 300 °C indicates amorphous characteristics (Fig. 3b), but peaks 1(2θ = 20.30°) and 2(2θ = 24.44°) are shown, due to diffractions from (001) planes of V_2O_5 and (210) planes of V_4O_9 phases, respectively. When the film was annealed at 500 °C, Fig. 3c shows peaks 1(2θ = 27.86°) and 2(2θ = 37.14°) that are related to (011) and (200) planes of VO_2 phase respectively. No other vanadium oxides are detected. In addition, the (011) peak is strong, but the (200) peak is weak. It indicates that the film has a strong orientation relation to the Si substrate, which may be either due to the lattice match between the film and the substrate [24]. The full width at half maximum (FWHM) of the (011) peak is narrow with a value of 0.42, implying high crystallinity of the film. The number of the observed peaks for the film annealed at 700 °C increases. Figure 3d shows peaks 1(2θ = 19.15°), 2(2θ = 33.89°), 3(2θ = 35.74°), 4 (2θ = 37.24°), 5(2θ = 40.76°), 6(2θ = 53.54°), 7 (2θ = 56.51°) and 8(2θ = 68.57°), which may be coincide with the diffractions from (200) planes of V_3O_5, $(\bar{3}11)$ planes of VO_2, (311) planes of V_6O_{13}, (200) planes of VO_2, $(\bar{4}11)$ planes of V_3O_5, (221) and (222) planes of V_6O_{13} and (611) planes of VO_2 phases, respectively. The variation in the XRD patterns is resulted from differences in the crystallinity of the films annealed at different temperatures.

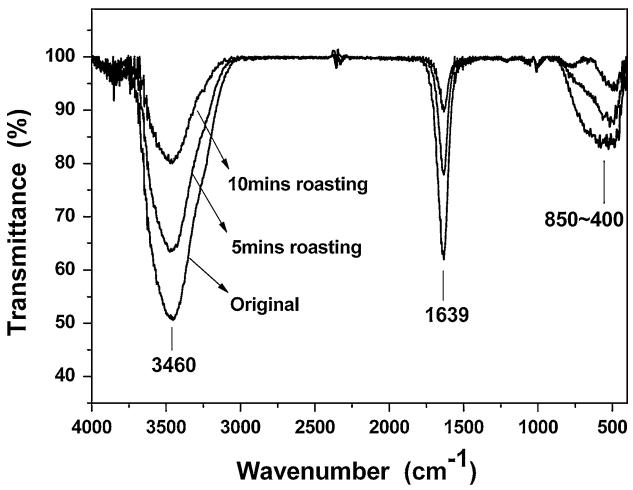

Fig. 2 FTIR spectrum of the V_2O_5 gel on KBr plates after different roasting time at 110 °C

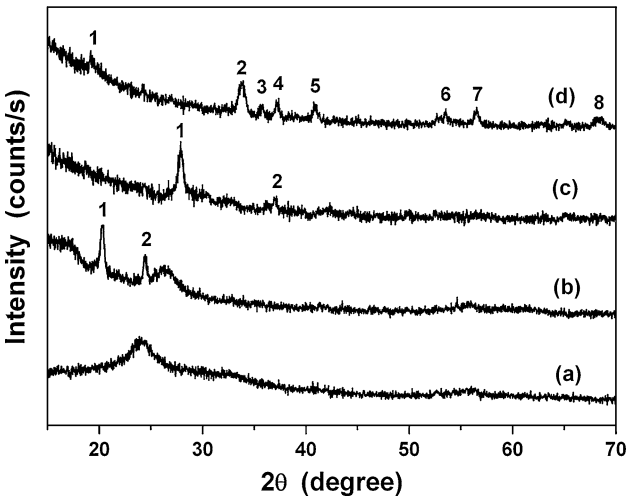

Fig. 3 XRD patterns of the VO_2 films annealed at (**a**) 110 °C, (**b**) 300 °C, (**c**) 500 °C and (**d**) 700 °C

Furthermore, concerning the phase transition of the VO_2 films illustrated in this work, the changes in temperature-controlled XRD patterns of the film annealed at 500 °C was shown in Fig. 4. The diffraction peak at $2\theta = 27.86°$ corresponds to the (011) planes of monoclinic VO_2 (taken at room temperature about 25 °C). But the peak shifts to a lower angle of $2\theta = 27.75°$ (taken at 90 °C above the phase transition temperature), with a tiny increase of the diffraction intensity. It is attributed to the changes of the film from monoclinic to tetragonal phase transition, which has been also illustrated in our previous paper [25].

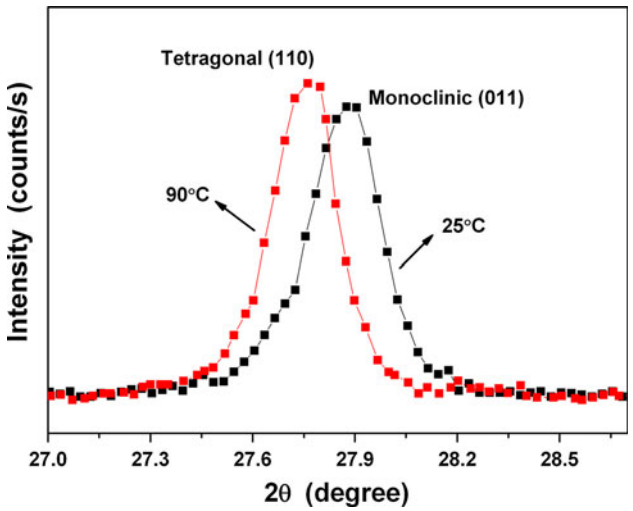

Fig. 4 Temperature-controlled XRD patterns of the film annealed at 500 °C, taken at 25 and 90 °C

3.4 FE-SEM and AFM

The morphology and microstructure of the films were further investigated by FE-SEM and AFM. Figure 5 shows the FE-SEM photographs for the films annealed at different temperatures. The film annealed at 110 °C (Fig. 5a) shows a flat surface. According to the former XRD results, we assume that the film was formed by the dry V_2O_5 gel film without crystallizing. Figure 5b exhibits the similar morphology, while extremely weak particles are formed at this annealing temperature (300 °C). Increasing annealing temperature at 500 °C resulted in more clear grain boundaries and grain growth. It is seen in the Fig. 5c that the surface of VO_2 film is uniform and compact with a grain size of about 120 nm. There are no obvious surface defects observed in

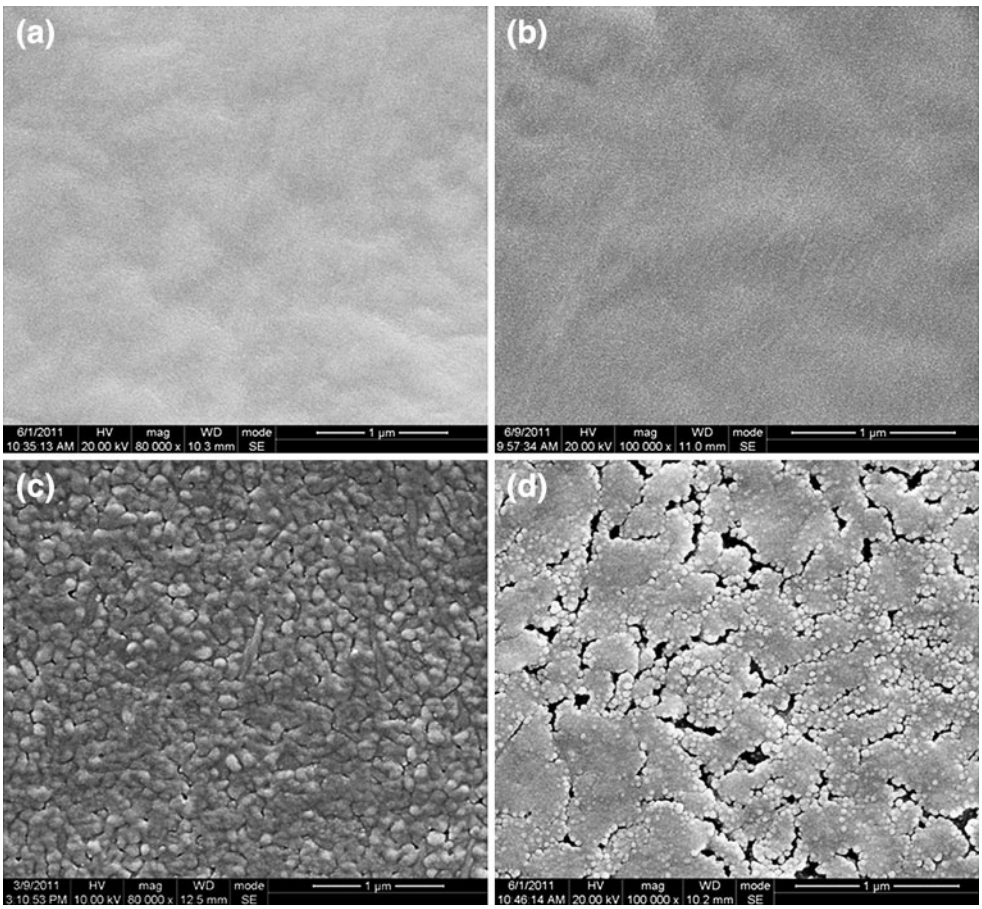

Fig. 5 SEM images of the VO_2 films annealed at (**a**) 110 °C, (**b**) 300 °C, (**c**) 500 °C and (**d**) 700 °C

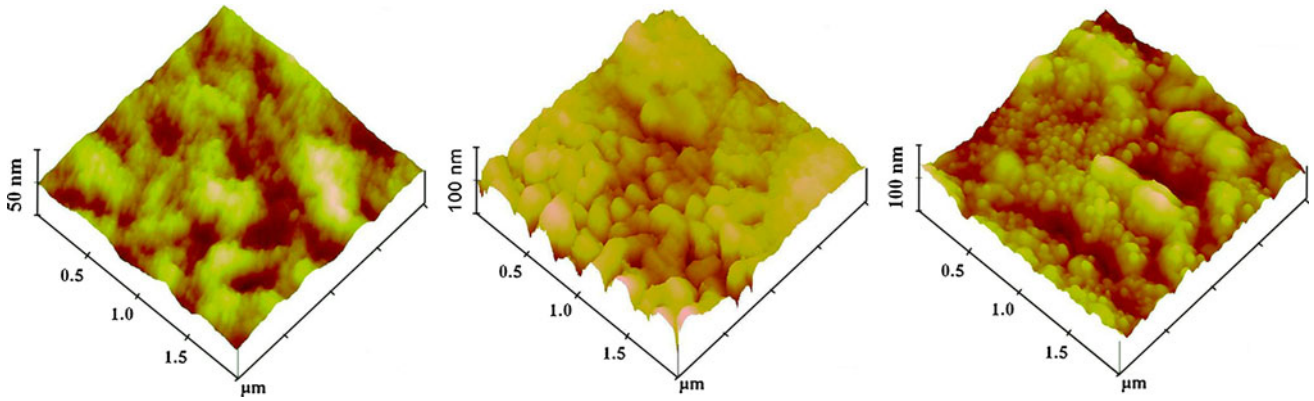

Fig. 6 AFM images of the VO_2 films annealed at (**a**) 300 °C, (**b**) 500 °C and (**c**) 700 °C

the image, which may be formed during the dip coating and drying process. But the film annealed at 700 °C shows obvious microcracks, due to the pronounced grain refinement. The microcracks are harmful for the phase transition properties of VO_2 films [26].

AFM image (Fig. 6) shows the area of 2 μm × 2 μm morphologies of the films annealed at 300, 500 and 700 °C. It suggests that the films underwent the grain growth, agglomeration and grain refinement process with increased annealing temperatures, as illustrated by FE-SEM photographs.

3.5 FT-IR in VO_2 thin films

Figure 7 shows a graph of transmittance against temperature at $\lambda = 25$ μm, the wavelength at which the sharpest contrast was observed bellow and above the phase transition temperature. The films annealed at 110 and 300 °C did not show any phase transition properties during the detecting temperature range from 30 to 90 °C, for there is no VO_2 phase existed. The transmittance for the film annealed at 700 °C decreases from 36.2 to 25.8% during the phase transition. The low variation could be attributed to the multiphase coexistence and the obvious microcracks. However, for the film annealed at 500 °C, the curve exhibits a decrease of transmittance from 35.5 to 2.5%. Moreover, as the derivative of the temperature dependence of transmittance (dTr/dT) (Fig. 8), the phase transition temperature of the film annealed at 500 °C could be evaluated to be 60.4 °C in the heating transition and 55.8 °C in the cooling transition. The significant decrease in transition temperature and hysteresis width of VO_2 film on Si has been attributed to either the compressive strain along [011] direction [27], or larger fraction of +4 valence vanadium [28].

As for the cycle stability, the repeated phase transition with 30, 50 and 100 times and the accompanied optical changes of the VO_2 film annealed at 500 °C were

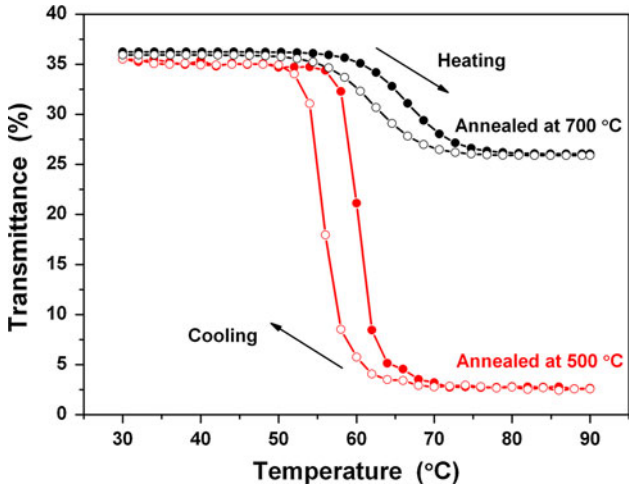

Fig. 7 Hysteresis curves of transmittance against temperature at 25 μm for the VO_2 films annealed at (**a**) 500 °C and (**b**) 700 °C

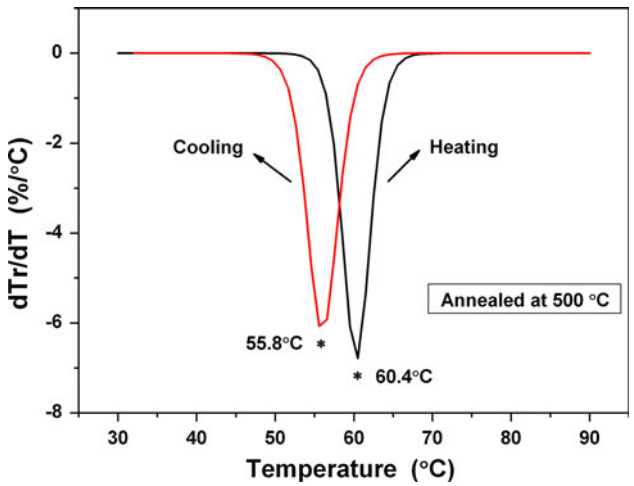

Fig. 8 Transition temperature of the VO_2 film annealed at 500 °C, determined during temperature ramping up and ramping down, respectively

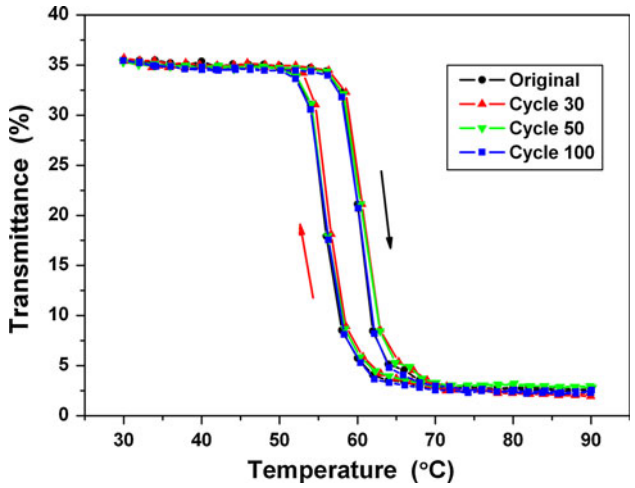

Fig. 9 Hysteresis curves of transmittance against temperature obtained for 30, 50 and 100 cycles in the VO_2 film annealed at 500 °C

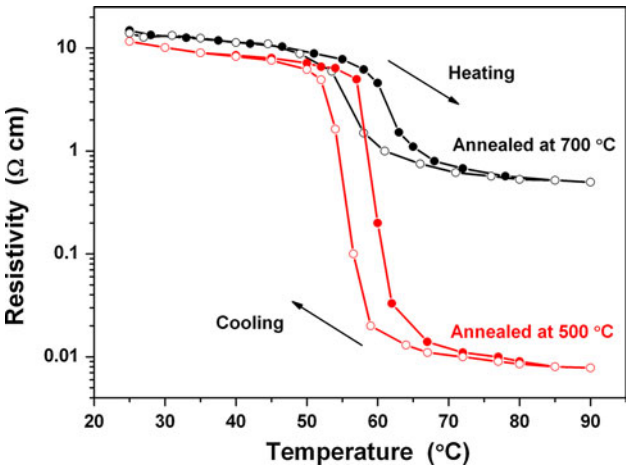

Fig. 10 Hysteresis curves of resistivity against temperature of the VO2 films annealed at (**a**) 500 °C and (**b**) 700°C

measured, shown in Fig. 9. The hysteresis curves of transmittance against temperature suggest that the thermal triggered change of transmittance at $\lambda = 25$ μm can revert back to its original value over a large number of cycles without deviations of the critical transition temperatures and hysteresis widths. The phase transition property of the VO_2 films appears to be able to remain stable during repetitive cycles. They would therefore be convenient for the variety of applications discussed earlier.

3.6 Resistivity

The electrical phase transition property of VO_2 film annealed at 500 °C and 700 °C were studied by the four-point probe method to record variations in resistivity with temperature (Fig. 10). A typical hysteresis cycle, similar to that of the FT-IR curves, was also observed. For the film annealed at 700 °C, the resistivity of the film drops from 14.9 Ω cm at 25 °C to 0.52 Ω cm above 75 °C. By contrast, the resistivity of the film annealed at 500 °C has an abrupt drop from 11.6 Ω cm at 25 °C to 0.01 Ω cm above 75 °C. The resistivity of the VO_2 film changes by more than 3 orders of magnitude when cycled through the phase transition. This amplitude of variation is also larger than the usually obtained change of 2–3 orders of VO_2 films.

4 Conclusions

In summary, we fabricated VO_2 thin films on single crystal Si (100) substrates by sol–gel method, including a process of annealing a vanadium pentoxide (V_2O_5) gel precursor at 110, 300, 500 and 700 °C. The Si substrate was pre-treated with hydrophilic solution and obtained an improved hydrophilicity. A decrease of contact angle from 68.0° to 12.1° resulted in a better contact performance between the film and Si substrate.

The film annealed at 110 °C is still amorphous, but the films underwent the grain growth, agglomeration and grain refinement process with increased annealing temperatures. The film annealed at 500 °C exhibits the formation of VO_2 phase with a strong (011) preferred orientation and high crystallinity, the surface of the film is uniform and compact with a grain size of about 120 nm. Meanwhile, the films annealed at 110 and 300 °C did not show any phase transition properties during the detecting temperature range from 30 to 90 °C, for there is no VO_2 phase existed. The transmittance for the film annealed at 700 °C decreases from 36.2 to 25.8% at $\lambda = 25$ μm during the phase transition. But the film annealed at 500 °C exhibits excellent phase transition properties, with a decrease of transmittance from 35.5% to 2.5% and more than 3 orders of resistivity magnitude variation bellow and above the phase transition temperature. The phase transition temperature is evaluated at 60.4 °C in the heating transition and 55.8 °C in the cooling transition. Furthermore, the phase transition property of the VO_2 film appears to be able to remain stable over repetitive cycles 100 times. These results indicate that the sol–gel method could be a suitable process for fabricating VO_2 film with excellent phase transition properties on Si substrate.

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